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Designing Resist Materials For Microlithography

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13. ABSTRACT (Maximum 200 words) The design of resist materials for microlithography has become more and more complex due to the ever increasing number of demands that are placed on these materials . In particular it is difficult to introduce new features or new chemistries in resists while still maintaining the "look and feel" and traditional behavior of well established materials. This presentation focuses on the chemistry of resists based on chemically amplified processes that are readily implemented in novel high performance materials. Both positive-tone and negative-tone imaging schemes are considered as is the development of environmentally friendly materials that obviate the use of organic solvents and can be coated and pro- cessed in a fully aqueous system. The importance of a full understanding of the the reac- tions mechanisms that regulate the performance of the resist is underlined.				
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Summary.

The design of resist materials for microlithography has become more and more complex due to the ever increasing number of demands that are placed on these materials. In particular it is difficult to introduce new features or new chemistries in resists while still maintaining the "look and feel" and traditional behavior of well established materials. This presentation focuses on the chemistry of resists based on chemically amplified processes that are readily implemented in novel high performance materials. Both positive-tone and negative-tone imaging schemes are considered as is the development of environmentally friendly materials that obviate the use of organic solvents and can be coated and processed in a fully aqueous system. The importance of a full understanding of the the reactions mechanisms that regulate the performance of the resist is underlined.

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The design of resist materials for microlithography has become more and more complex due to the ever increasing number of demands that are placed on these materials [1]. The long-established requirements of sensitivity, resolution, and etch resistance [2] still exist today, but as new generations of more powerful and complex electronic devices are produced, the properties "wish-list" of production engineers keeps growing and more features and properties are assumed to be readily available. To the resist chemist, this "wish-list" soon translates into a "must-have list". Particularly troublesome is the common unwritten requirement that a new material should possess vastly enhanced properties while maintaining the "look-and-feel" of the old material. As a result, excellent materials may fail to be considered seriously simply because they do not behave *quite like* the old familiar industry standard, or because they do not meet what may be obsolete or unnecessary requirements. Clearly this issue is different if considered from the production engineer's point of view since failure on the production line is simply not a viable option! Nevertheless, as the current generation of UV photoresists and imaging tools reaches its ultimate performance and as new environmental issues continue to emerge, it is clear that some radical options may have to be considered. Even if one assumes that the intrinsic performance of the resists is not an issue, will today's solvents, gas and liquid effluents, be acceptable to-morrow?

From a chemistry point of view, the challenges can be separated into several broad categories:

- (i) radiation chemistry of the materials,
- (ii) physical, chemical, and mechanical properties of the resists,
- (iii) environmental acceptability of the materials and processes used to form the resist coating, then develop and transfer the image.

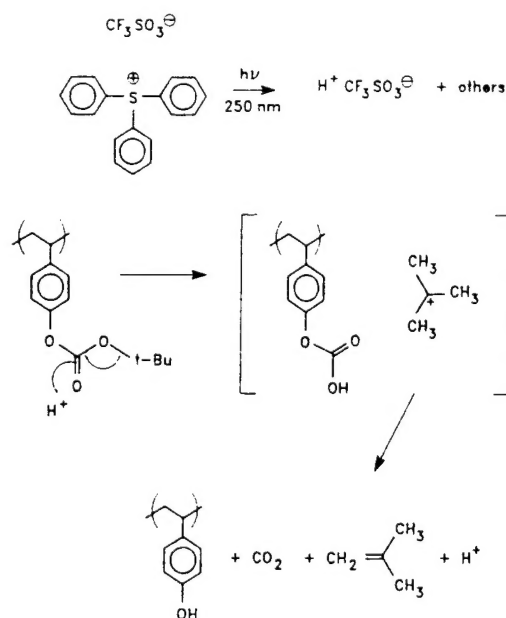


Figure 1. The poly(t-BOC-styrene) resist.

Radiation Chemistry.

Today, the most widely used resists for microlithography are based on the novolac-diazonaphthoquinone developed in the Kalle laboratories more than four decades ago [3]. The first chemically amplified resist based on a poly(t-BOC-styrene)-onium salt combination [4] shown in Figure 1 was used only in 1985 by IBM engineers for the commercial manufacture of 1 megabit chips [5]. These two important families of materials have fundamentally different types of chemistries that are remarkable for their efficiencies and can serve as models for future resist designs. Although other materials were also developed during the three decades that separate these two inventions, few have had a lasting impact in practical microlithography.

The novolac-diazonaphthoquinone resists owe their remarkable features and longevity to the unique combination of good properties (adhesion, solubility, etch resistance, etc.) of the novolac resin and the very efficient photochemistry of the diazonaphthoquinones. Unfortunately, few photochemical reactions have such efficiency, and fewer still could be of conceivable use in the design of a resist material. Therefore, even if one ignores the "look and feel" issue, it is difficult to envision the replacement of the diazonaphthoquinones by moieties that surpass them in terms of photochemical performance.

In contrast, the poly(t-BOC-styrene)-onium salt combination is, in theory at least, much easier to duplicate [1]. The basic concept that underlies all chemically amplified resists today is that radiation is not used to perform a multiplicity of chemical reactions as is the case with diazonaphthoquinone resists. Instead, radiation is used only for a very limited number of chemical reactions that generate a catalyst (acid) within the polymer coating. Once this acid has been generated - a process that delineates the latent image - a thermal "bake" step can be used to provide the system with the activation energy that is required for the catalyst to perform its action on the polymer in which it is dispersed. Because it is the catalyst, and not the radiation, that modifies the polymer film, the process is chemically amplified: very few photochemical events generate the catalyst that, in turn, modifies extensively the polymer.

Chemical amplification

Since many chemical reactions are subject to catalysis, the chemical amplification route appears to be the most desirable for the design of novel resists with enhanced or uniquely designed properties. A survey of common organic chemical reactions reveals that the most frequently used catalysts are acids, bases, or metal complexes. The photogeneration of acid is well known from the excellent work of Crivello and others [6]. For example triarylsulfonium salts or diaryliodonium salts are known to be efficient sources of strong acid under a variety of irradiation conditions (light, E-beam, X-ray). In contrast, the photogeneration of base is less well developed although Cameron and Fréchet [7], Kutal and Willson [8] and Yamaoka et al. [9] have described several interesting precursors of relatively weak bases such as amines. Because the photogeneration of metal complexes with catalytic properties is not a well developed area, these types of catalysts are unlikely to have an impact on resist development until early in the next decade.

Numerous chemically amplified systems based on radiation generated acid have been developed successfully [1, 10] and several based on modifications of the original poly(t-BOC-styrene)-onium salt system have been commercialized. In contrast chemically amplified resists that utilize photogenerated base are still laboratory curiosities and none appear likely to be commercialized soon.

The reasons for this discrepancy rest not only on the fact it is easier to generate acid by irradiation than it is to generate base, but also on the ready availability of a wealth of acid-catalyzed reactions that can be used to design new resist materials.

It is for these reasons that the following will describe two approaches to state-of-the-art resist materials involving photo-generated acid that demonstrate the versatility of designs based on chemical amplification.

Design of a negative-tone resist.

Negative-tone resists based on the acid-catalyzed cross-linking of a polymer may be designed using common reactions such as electrophilic additions. For imaging in the deep-UV (ca. 250nm) a polymer such as poly(hydroxystyrene) that has a high transmission at the exposure wavelength and is both soluble in aqueous base and resistant to etching is selected. In addition to the acid photogenerator [6] a polyfunctional crosslinker that can participate in acid-catalyzed electrophilic aromatic substitution with the polymer is required to complete the three-component resist. Simple considerations of carbocation stability may then be used to optimize the system and to tune the resist sensitivity to the desired level. Typically, the higher the stabilization of the cationic intermediates, the higher the sensitivity of the resist. Our recent studies [11] with such systems have demonstrated that a good mechanistic understanding of the chemical amplification process goes a long way towards achieving resist optimization.

Figure 2 shows a number of crosslinkers that may be used in combination with poly(hydroxystyrene) and a photoacid generator such as triphenylsulfonium triflate to afford resists with deep-UV sensitivities in the range 0.1-20 mJ/cm². The versatility of these materials also allows them to be used efficiently with E-beam or X-ray radiation.

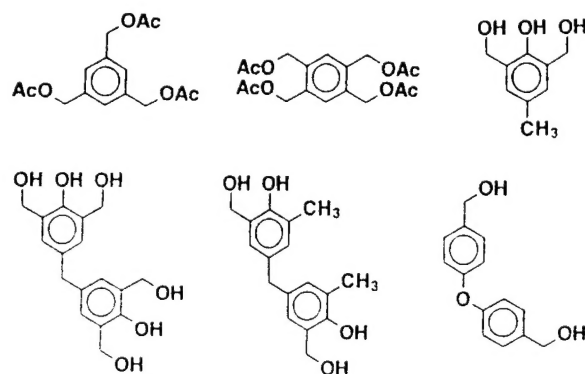


Figure 2. Crosslinkers for chemically amplified resists

Design of a positive tone resist

The design of chemically amplified positive-tone resists is much more difficult than that of negative-tone resists because the need to increase polymer solubility in exposed areas of the film generally requires that a high extent of reaction be achieved. A clue for the design of new positive-tone resists may be taken from the classic novolac-diazonaphthoquinone systems in which the solubility of the exposed areas of the films is increased through the transformation of the diazonaphthoquinone moieties into highly soluble indene-carboxylic acid. We have now designed a new family of dissolution inhibitors that can be transformed into highly base-soluble materials (Figure 3) via a chemically amplified process that involves photogenerated acid [12].

The sensitivity of these materials is also high and it can be tuned on the basis of structural and mechanistic considerations. In addition, because radiation generated acid is used in the key imaging step, these new materials can be used in combination with other substrates such as novolac, or for imaging with E-beam or X-ray radiation [12].

The design of environmentally friendly resist materials.

Because it is generally acknowledged that the most environmentally benign solvents should be used in the production clean rooms, it is important to seek fundamentally new resist

systems that are compatible for example with a totally aqueous process. We have initiated a search for the various components that might be incorporated into such resists. In a first step, we have determined that innocuous polyfunctional compounds such as the sugars glucose or xylose can be used as efficient crosslinkers in the formulation of chemically amplified resists [13]. Current research focuses on novel resins and catalyst precursors that are soluble in water, as well as processes for imaging in both the positive and negative tone modes. It is expected that, in addition to microlithography, such water-soluble resists could impact applications such as the manufacture of circuit boards or active matrix display for which lower resolutions are required.

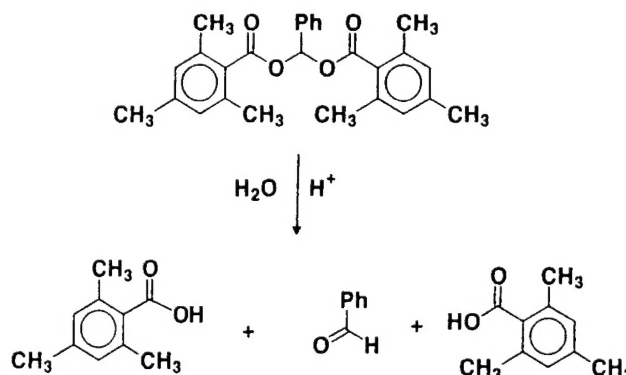


Figure 3. Chemistry of the dissolution inhibitors.

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